Supplementary Material for:

"Hydrothermal Friedel-Crafts Type Alkylation of Phenols with Alcohols in Diluted Acids"

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The following tables list the amounts of detected reaction products (as determined by GC-FID unsig toluene as an internal standard) obtained in the hydrothermal alkylation of phenol (15 mmol) with benzyl alcohol (0.5mmol) after 16h of reaction. The following figure gives the label of the various obtained molecules

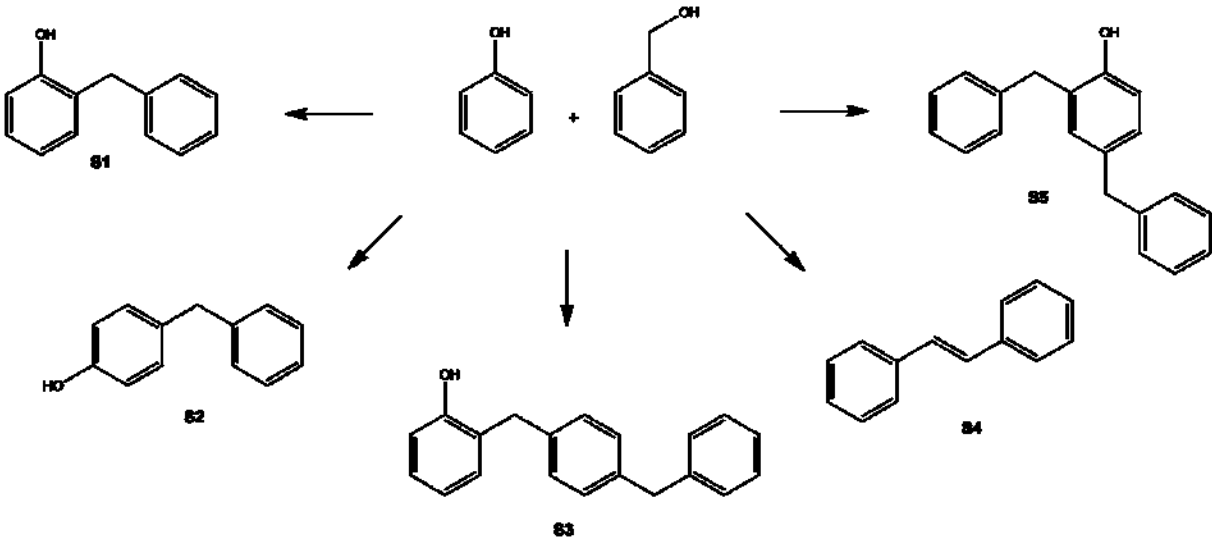

Table S1: Alkylation of phenol with benzyl alcohol in aqueous media.

solvent	temperature	benzyl alcohol	S1	S2	S3*	S4	S5	o/p-ratio (mono-substituted product)
	125°C	100%	0%	0%	0%	0%	0%	-
	150°C	100%	0%	0%	0%	0%	0%	-
	180°C	99%	1%	0%	0%	0%	0%	-
	200°C	93%	4%	3%	0%	0%	0%	61:39
water	220°C	86%	8%	6%	0%	0%	0%	59:41
	125°C	0%	44%	44%	3%	3%	6%	50:50
	150°C	1%	38%	35%	9%	4%	14%	52:48
	180°C	0%	35%	31%	12%	2%	20%	53:47
	200°C	0%	36%	31%	12%	1%	20%	53:47
0.5M HCl	220°C	0%	33%	30%	13%	2%	22%	53:47
	125°C	16%	34%	37%	4%	3%	6%	48:52
	150°C	0%	37%	37%	9%	2%	15%	50:50
	180°C	0%	35%	34%	12%	1%	19%	51:49
	200°C	6%	34%	32%	11%	1%	17%	51:49
1M HCl	220°C	0%	32%	30%	13%	1%	23%	52:48

Normalized results after 16h at different temperatures. *) There are two isomers of benzyl benzyl phenol.]

Table S2: Alkylation of phenol with benzyl alcohol: Variation of the acids.

acid	concentration	**benzyl alcohol**	**S1**	**S2**	**S3***	**S4**	**S5**	**o/p-ratio (mono-substituted product)**
HCl	1M	0%	35%	34%	11%	1%	19%	51:49
HCl	0.5M	0%	35%	31%	12%	2%	20%	53:47
HCl	0.4M	0%	34%	30%	14%	2%	20%	53:47
HCl	0.3M	0%	35%	30%	13%	2%	20%	53:47
HCl	0.2M	0%	34%	29%	14%	3%	20%	54:46
HCl	0.1M	0%	34%	28%	14%	4%	20%	55:45
HCl	0.05M	1%	33%	27%	14%	4%	20%	55:45
HCl	0.04M	1%	33%	27%	14%	4%	20%	55:45
HCl	0.03M	2%	33%	27%	14%	4%	19%	55:45
HCl	0.02M	6%	33%	26%	13%	4%	18%	55:45
HCl	0.01M	17%	29%	23%	12%	4%	15%	56:44
HCl	0.005M	31%	28%	22%	7%	2%	9%	56:44
HOAc	1M	53%	23%	17%	3%	0%	4%	58:42
HOAc	0.5M	51%	25%	19%	2%	0%	3%	57:43
HOAc	0.25M	72%	15%	11%	0%	0%	1%	58:42
HOAc	0.1M	79%	12%	9%	0%	0%	0%	58:42
HOAc	0.05M	84%	9%	7%	0%	0%	0%	59:41
HCOOH	1M	14%	32%	25%	11%	3%	15%	56:44
HCOOH	0.5M	28%	29%	22%	8%	2%	10%	56:44
HCOOH	0.25M	42%	26%	20%	5%	0%	7%	56:44
HCOOH	0.1M	56%	21%	16%	2%	0%	4%	57:43
HCOOH	0.05M	66%	18%	14%	0%	0%	2%	57:43

Normalized results after 16h at 180°C. Obviously not all the benzyl alcohol was detected for 0.5M HOAc. *) There are two isomers of benzyl-benzyl phenol.